Sampling and Analytical Protocols for Monitoring PCBs in Effluent and Storm Water

Mark Richards

VA Dept. of Environmental Quality

January 8, 2008

Discussion Topics

- Standard Operating Procedures
  - Sample collection
  - Guidance - Appendix B
- Analytical Overview/Requirements
  - Guidance - Appendix C
- Reporting Requirements
  - Data Submittal

Pt. Source PCB Monitoring for TMDL development

- Data Quality Objectives
  - Sample identification (Guidance)
  - Sample size and collection methods
  - Analytical methodology, including specific modifications
  - Electronic data formatting and reporting

Pt. Source PCB Monitoring for TMDL development

- Sample Collection Methods – Appendix B
  - Consistent collection of samples using clean techniques
  - Allow flexibility
    - Permit holders determine approach for collecting samples
  - Cost containment

PCB Monitoring Options

- Twenty-four hour composite samples
  - Applicable only to continuous flowing outfalls
  - Automated sampler
  - More costly
- Instantaneous grab samples
  - Applicable to all outfall types (continuous, intermittent, storm water)
  - Cheaper alternative

24hr Composite Samples

- Based on approach developed for Delaware Bay PCB study
  - Applied to Potomac & Roanoke River point sources
- 24-hour time-weighted composites (flow-weighted also ok)

24hr Composite Samples

- Ultra-clean sampling
  - Requires new Teflon lined tubing
  - Solvent rinsed
  - All other equipment solvent rinsed
- Equipment rinsate blank required
  - PCB free DI water obtained from lab
- Certified clean amber glass bottles
  - PCB free (obtained from lab)
- Sample volume = 2 Liters
- Compliance monitoring pt

Instantaneous Grab Samples

- May consist of 1 or more samples
- Option available to collect 2 or more grab samples (Indus. SW excluded)
  - Referred as “Manual Composite”
  - Consist of equal aliquots of sample collected at pre-determined intervals over a 24h time period (e.g., 4, 6, 8 or 12 hours)
  - Must be composited within the analytical laboratory

Instantaneous Grabs

- Total Volume = 2 Liters
  - Collect 2 – 1 Liter samples, 4 - 0.5 Liter samples, etc.
  - Certified clean amber glass bottles
- Compliance monitoring point

Dry vs Wet Samples

- Municipal waste & industrial process waste (that combines w/storm water).
  - Dry condition defined as no measurable (< 0.1 inch) rainfall in 72h period.
  - Wet condition defined as rain event that exceeds 0.1 inch and results in an increase in wastewater flow.
    - Guideline – wet weather event (>0.1 inch) and at least a 10% increase in influent flow
      - Also take into account plant retention

Industrial Storm Water

- As defined in 9 VAC 25-151-10
- Instantaneous grab samples
  - A single 2-L sample per event
- Collected within first 30 minutes of the discharge (or within the first hour if impracticable).
- Event must be at least 0.1 inch and collected > 72h from previous measurable event.

PCB Samples

- Sample Preservation
  - Chill to $\leq 4^{o}$ C and keep in the dark
- Holding time up to one year
  - Lengthy holding time allows batch analysis
  - Laboratories offer volume discounts
    - Can run in lots of 20 samples
- Shipping Samples
  - Bubble wrap bottles
  - Cooler containing bagged wet ice or Blue Ice

PCB Analysis

PCB Analytical Method

- EPA Method 1668, Revision A
  - High Resolution GC/ High Resolution MS
  - Analyzes 209 Congeners
  - Low detection (5-10 pg/L per congener)
  - Performance based method
- Guidance document – Appendix C
  - Consistent application of method by qualified laboratories

EPA Method 1668A

- Method Summary
  - Isotope dilution quantitation
    - 12 toxic WHO congeners
    - Earliest and latest eluting congener at each level of chlorination (homolog group)
      - ^{13}C labeled analogs
  - All other congeners quantitated using the internal standard quantitation technique

EPA Method 1668A

Method Summary (aqueous samples)

- Extraction
  - 2-L sample size extracted with methylene chloride using SPE, Separatory Funnel or CLLE
- Sample Clean-up (not always needed)
  - Back-extraction with sulfuric acid and/or base, and GPC, silica gel, or Florisil
- Extract Concentration
  - Solvent reduced to 20 µl
- Analysis
  - HRGC/HRMS with quantitation by isotope dilution and internal standard technique

Analytical Requirements

- Extraction and Cleanup
  - All OPR samples, method blanks, field blanks or other QC samples must be processed identically to the effluent samples
- Column/Retention Time Calibration
  - The use of a SPB-octyl column is recommended (DB5 column also used)

Analytical Requirements

- Initial Calibration
  - Minimum of 5 levels for each of the toxic WHO or level of chlorination congeners
- Low calibration standard is 1.0 ng/ml
  - DRBC requires 0.5 ng/ml
    - May consider but have not found to be commercially available

Analytical QC Requirements

Analytical labs adhere to QC requirements

- VER – calibration verification
  - Beginning of each work shift
  - Meet requirements of method
- OPR – On-going precision and Recovery
  - Required for each batch
  - Surrogate recovery
  - Meet requirements of method
- Method blanks
  - Meet requirements of decision rules

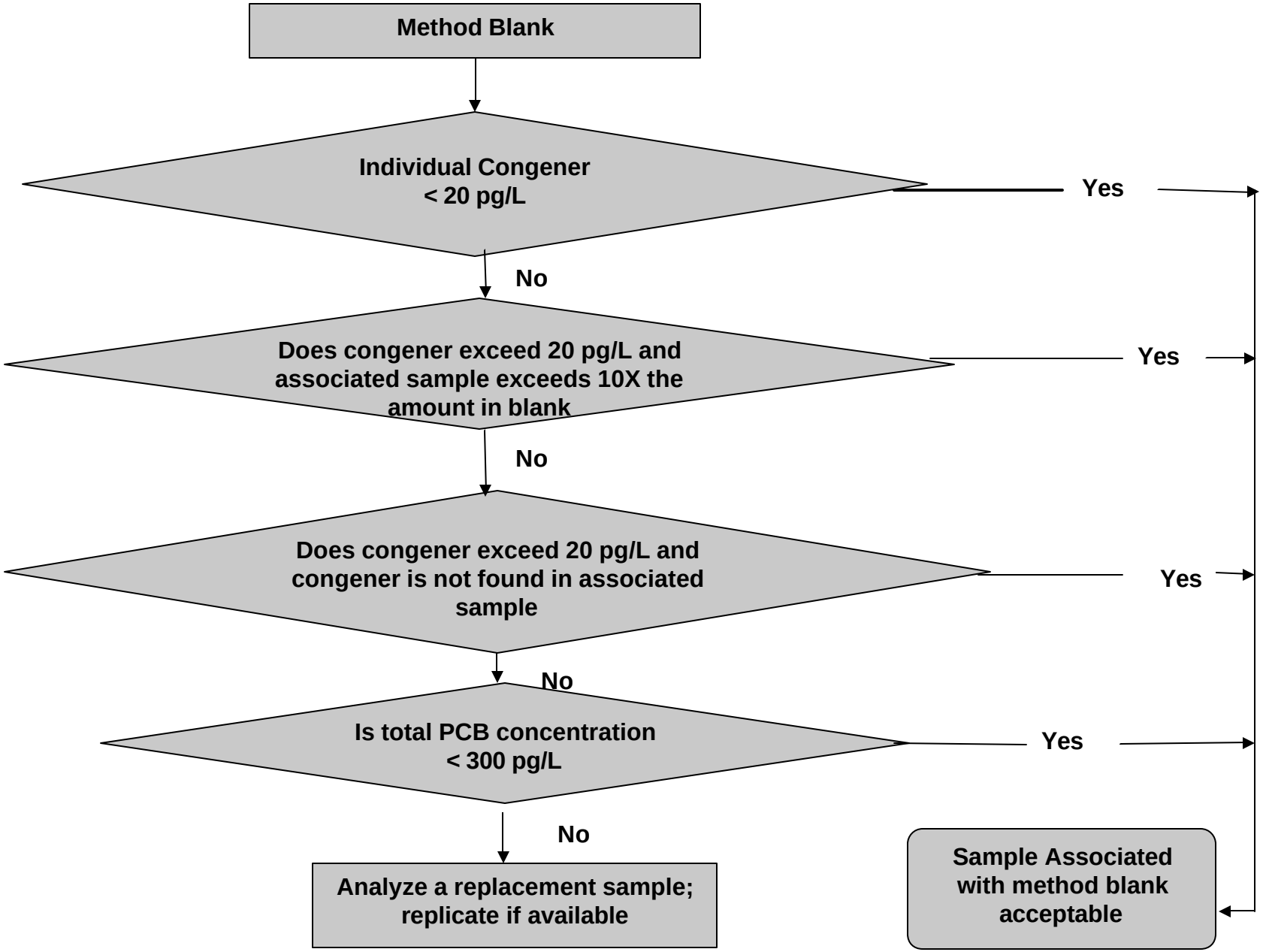
PCB Reporting

- Method specifies how to attain Est. Min. Detection Level (EMDL) and Est. Min. Level (EML) per congener.
  - MLs based on the LCL
  - Based on low blank contamination

$$\text{EML (QL)} = \frac{(1000 \text{ pg/ng}) \times (1 \text{ ng/mL}) \times (0.02 \text{ mL})}{2 \text{ L}} = 10 \text{ pg/L}$$

- Consistent with permit program
  - QL = the lowest concentration used for the calibration of a measurement system when the calibration is in accordance with method.

Method Blank Contamination Decision Rules



Data Qualifiers

- Can be found in Guidance Appendix C, Attachment 3.
  - More common data qualifiers
    - J – below reporting level but above detection level
    - U – not detected at est. detection level
    - B – analyte in sample and associated blank
    - V – surrogate recovery not within limits
    - EMPC – Est. maximum possible conc. (peak detected but not at required criteria)

Data Reporting/Submittal Requirements

- Electronic Data Format
  - Sample collection information
  - Chain of Custody
  - Report all 209 congeners
    - Co-eluting Congeners
    - Qualify data when necessary
    - Associated QA/QC data
- Work in Progress (1-2 months)
  - Simple spreadsheet
  - DRBC prototype

Questions